

AFOSR-TR-96

6075

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

FINAL REPORT

for

Contract Number F49620-93-1-0110

**PHOTOFRAGMENTATION SPECTROSCOPY AND
PHOTODISSOCIATION DYNAMICS OF POLYATOMIC MOLECULES**

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March 1, 1996

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REPORT DOCUMENTATION PAGE

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OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)			2. REPORT DATE 96 MAR	3. REPORT TYPE AND DATES COVERED Final 93 JAN 01-95 DEC 31	
4. TITLE AND SUBTITLE Photofragmentation Spectroscopy and Photodissociation Dynamics of Polyatomic Molecules			5. FUNDING NUMBERS F49620-93-1-0110 61102F 2300/HS		
6. AUTHOR(S) Brad R. Weiner			8. PERFORMING ORGANIZATION REPORT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Puerto Rico Department of Chemistry Box 23346 UPR Station Río Piedras, PR 00931			10. SPONSORING / MONITORING AGENCY REPORT NUMBER		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR / WL Building 410 Bolling AFB, DC 20332-6448 Dr. Herman			12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release Distribution is Unlimited		
11. SUPPLEMENTARY NOTES			12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) The detailed reaction dynamics of several gas phase polyatomic systems has been established in this research at the Department of Chemistry at the University of Puerto Rico. Real time dynamics of sulfur monoxide photoelimination reactions have been studied by laser induced fluorescence spectroscopy of the nascent SO fragment on the $B^3\Sigma^- - X^3\Sigma^+$ transition in the region of 237-310 nm. The following group of molecules has been studied: Sulfur dioxide (SO_2), the thionyl halides (SOX_2 , where $X=\text{F}, \text{Cl}$ or Br), dimethyl sulfoxide ($(\text{CH}_3)_2\text{SO}$), ethylene episulfoxide ($(\text{CH}_2)_2\text{SO}$), trimethylene sulfoxide ($(\text{CH}_2)_3\text{SO}$), tetramethylene sulfoxide ($(\text{CH}_2)_4\text{SO}$), and thionyl aniline ($\text{C}_6\text{H}_5\text{NSO}$). In all of these experiments, the parent molecule is irradiated with an excimer laser (either 193 or 248 nm) and the energy disposal into the nascent SO photofragment is determined, and used as a mechanistic probe. A broad picture of sulfur monoxide photoelimination reactions emerges from this work. A general procedure to evaluate the rotational state population distributions of the nascent photofragments from the photodissociation of polyatomic molecules has been implemented with the use of a kinematic distribution function. Numerical evaluations of rotational state population distributions of diatomic photofragments from photodissociation of the general class of triatomic molecules are presented. In a second area, the photophysics and photochemistry of the vinoxy radical were investigated. Fluorescence decay rates were determined in the presence of twelve collision partners: He, Ar, N ₂ , O ₂ , CO, H ₂ , HCl, CO ₂ , N ₂ O, C ₂ H ₄ , SF ₆ and CH ₃ OCH=CH ₂ . The measured electronic quenching cross-sections vary from 0.01 - 66.5 Å ² . A vibrational level dependence was found for the radiative lifetimes. A kinetic model, consistent with all the experimental observations has been postulated. Several new transitions of the CH ₂ CHO (B-X) transition have been discovered. Finally, a study of bimolecular reactions has been initiated. O(³ P) reactions with several sulfides (OCS and C ₂ H ₄ S) have been studied by monitoring the product energy disposal in the sulfur monoxide fragment. Both of these reactions are found to proceed by abstraction of the sulfur atom.					
14. SUBJECT TERMS Photodissociation Dynamics			15. NUMBER OF PAGES		
16. PRICE CODE					
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
20. LIMITATION OF ABSTRACT					

ABSTRACT

The detailed reaction dynamics of several gas phase polyatomic systems has been established in this research at the Department of Chemistry at the University of Puerto Rico. Real time dynamics of sulfur monoxide photoelimination reactions have been studied by laser induced fluorescence spectroscopy of the nascent SO fragment on the $B^3\Sigma^-$ - $X^3\Sigma^-$ transition in the region of 237-310 nm. The following group of molecules has been studied: Sulfur dioxide {SO₂}, the thionyl halides {SOX₂; where X=F,Cl or Br}, dimethyl sulfoxide {(CH₃)₂SO}, ethylene episulfoxide {(CH₂)₂SO}, trimethylene sulfoxide {(CH₂)₃SO}, tetramethylene sulfoxide {(CH₂)₄SO}, and thionyl aniline {C₆H₅NSO}. In all of these experiments, the parent molecule is irradiated with an excimer laser (either 193 or 248 nm) and the energy disposal into the nascent SO photofragment is determined, and used as a mechanistic probe. A broad picture of sulfur monoxide photoelimination reactions emerges from this work. A general procedure to evaluate the rotational state population distributions of the nascent photofragments from the photodissociation of polyatomic molecules has been implemented with the use of a kinematic distribution function. Numerical evaluations of rotational state population distributions of diatomic photofragments from photodissociation of the general class of triatomic molecules are presented. In a second area, the photophysics and photochemistry of the vinoxy radical were investigated. Fluorescence decay rates were determined in the presence of twelve collision partners: He, Ar, N₂, O₂, CO, H₂, HCl, CO₂, N₂O, C₂H₄, SF₆ and CH₃OCH=CH₂. The measured electronic quenching cross-sections vary from 0.01 - 66.5 Å². A vibrational level dependence was found for the radiative lifetimes. A kinetic model, consistent with all the experimental observations has been postulated. Several new transitions of the CH₂CHO (B-X) transition have been discovered. Finally, a study of bimolecular reactions has been initiated. O(³P) reactions with several sulfides (OCS and C₂H₄S) have been studied by monitoring the product energy disposal in the sulfur monoxide fragment. Both of these reactions are found to proceed by abstraction of the sulfur atom.

I. OBJECTIVES OF THE RESEARCH EFFORT

The objectives of this research effort were:

- (1) The development of an experimental program in gas phase photochemistry, unimolecular dissociation dynamics, and photofragmentation spectroscopy of polyatomic molecules.
- (2) To provide a more detailed understanding of the unimolecular dissociation dynamics of polyatomic molecules, includings sulfides, sulfur oxides, and free radicals of practical interest.
- (3) To extend the established methods of photodissociation dynamics for closed shell species to open-shell species, *i.e.* polyatomic free radicals.
- (4) Initiate a research program in mainstream physical chemistry at a minority institution, and provide a strong educational environment for students, both graduate and undergraduate.

II. ACCOMPLISHMENTS OF THE RESEARCH EFFORT

This research effort was initiated January 1, 1993, and we believe that the project has reached or at least made significant advances towards the stated goals. The project was a followup to another grant with the Air Force Office of Scientific Research: *Photodissociation Studies of Polyatomic Free Radicals* (Contract Number F49620-89-C-0070), and also works closely in conjunction with a Department of Defense EPSCoR award, *Photodissociation Studies of Sulfur Oxides* (AFOSR Contract Number F49620-92-J-0406) During the course of the contract, numerous accomplishments and goals have been achieved and reported. Now at the end of 3 years (the term of the contract), we report on the extent of the accomplishments, and how well these results met the stated objectives

In developing our program in gas phase photochemical dynamics of polyatomic molecules, we have done (and continue to do) a body of experimental studies on sulfur monoxide (SO) photoelimination reactions. This work was motivated by the importance of sulfur oxides in atmospheric and combustion environments, and was co-supported by a second AFOSR award. The

following group of molecules has been studied: Sulfur dioxide {SO₂}, the thionyl halides {SOX₂; where X=F,Cl or Br}, dimethyl sulfoxide {(CH₃)₂SO}, ethylene episulfoxide {(CH₂)₂SO}, trimethylene sulfoxide {(CH₂)₃SO}, tetramethylene sulfoxide {(CH₂)₄SO}, and thionyl aniline {C₆H₅NSO}. In all of these experiments, the parent molecule is irradiated with an excimer laser (either 193 or 248 nm) and the energy disposal into the nascent SO photofragment is determined, and used as a mechanistic probe. What follows is a brief description of the results found for each of these molecular systems.

II.1. SO₂

Due to the large number of studies on the 193 nm photodissociation of sulfur dioxide, we used this system primarily as a test of our laser induced fluorescence (LIF) technique. Our work, however, led us to some interesting discoveries and discrepancies with past work on the 193 nm photodissociation of SO₂. We therefore embarked on a reinvestigation of the photodissociation dynamics of SO₂. We have measured the nascent vibrational, rotational, and spin-state distributions of the SO(X³Σ) fragment in both a bulb and in a pulsed supersonic nozzle following 193 and 210 nm irradiation of SO₂. The 210 nm laser light was obtained by Raman shifting the ArF excimer laser transition to the first Stokes line in hydrogen gas. Our vibrational distribution following 193 nm photolysis was consistent with past measurements (not by LIF), giving us confidence in our experimental methods. The SO vibrational distribution at 210 nm is found to peak at v"=1. We do find differences in the rotational state distributions obtained in the bulb vs. free jet experiments, which is surprising for the predissociative nature of sulfur dioxide. We have also discovered an interesting spin polarization effect in the nascent SO photofragment, that varies with vibrational level, and appears to have a strong J dependence. The bimodal rotational distributions have been modelled using our kinematic distribution model (see below), and suggest that there are two crossing points for the predissociation of SO₂. These more detailed results on the photodissociation of SO₂ are being prepared for publication in the *Journal of Chemical Physics*.

II.2. Cl₂SO

Due to our extremely sensitive and quantum specific capabilities for the detection of SO(X³Σ), we have studied the photodissociation dynamics of thionyl halides. The photodissociation

of thionyl chloride (Cl_2SO) is of interest as a model system to study three-body fragmentation processes, which can occur either in concert or stepwise. The photodissociation of this tetratomic molecule at 193 and 248 nm has been studied by laser induced fluorescence spectroscopy of the nascent SO fragment on the $\text{B}^3\Sigma^+ - \text{X}^3\Sigma^+$ transition in the region of 237-295 nm. Photolysis of Cl_2SO at 193 nm leads to an inverted vibrational distribution for the nascent $\text{SO}(\text{X}^3\Sigma^+)$ with a population maximum at $v''=2$. The quantum yield, $\Phi_{\text{SO}(\text{X})}^{193\text{ nm}} = 0.73 \pm 0.10$, has been measured by comparison of the $\text{SO}(\text{X}^3\Sigma^+)$ produced from SO_2 . The results indicate a concerted three-body fragmentation mechanism as the primary dissociation channel. A Franck-Condon/golden rule model elucidates the geometry prior to the fragmentation and suggests a direct dissociation mechanism. The rotational and spin state distributions have been measured from the rovibronically resolved spectra to support our model of the detailed dissociation mechanism. At 248 nm, the nascent vibrational distribution was found to be bimodal. The vibrational state population distribution in $v''=0-2$, which accounts for most (~94%) of the nascent $\text{SO}(\text{X}^3\Sigma^+)$ population, was found to be thermal ($T_{\text{vib}}=1000 \pm 200\text{K}$), suggesting a stepwise fragmentation process. About 6% of the nascent SO population has been observed in other vibrational levels ($v''=3-7$), and most likely originates from the molecular elimination of Cl_2 from Cl_2SO .

These results provide important evidence of wavelength dependent photolysis channels in polyatomic molecules, and go further in characterizing them in microscopic detail. The original premise of Cl_2SO being a good model for polyatomic photodissociation dynamics studies is borne out. This work was published in the *Journal of Physical Chemistry* (J. Phys. Chem. 97, 1993, 12260).

II.3. F_2SO

The vibrational and rotational state distributions and the primary quantum yield of the $\text{SO}(\text{X}^3\Sigma^+)$ fragment following the laser photolysis of F_2SO at 193 nm have been measured by using laser induced fluorescence spectroscopy on the $\text{SO}(\text{B}^3\Sigma^+ - \text{X}^3\Sigma^+)$ transition. Molecular elimination of F_2 is the only energetically-allowed channel to produce the SO fragment. The quantum yield measurement, $\Phi_{\text{SO}(\text{X})}^{193\text{ nm}} = 0.06 \pm 0.01$, suggests that other photochemical channels, *i.e.*, $\text{FSO} + \text{F}$, must be operative as well. The vibrational distribution of the nascent $\text{SO}(\text{X})$ fragment has been found to be inverted with a population maximum at $v'' = 2$, indicating a rapid dissociation process, and suggests that the nascent F_2 fragment is born with significant vibrational excitation. A Franck-Condon model best fits the observed vibrational state distribution when the SO bond length is similar

to that of the ground state F₂SO. For more details on this work, see the full publication in *Chemical Physics Letters* (Chem. Phys. Lett. 216, 1993, 537).

In our attempts to fully understand the photochemistry of F₂SO, we are seeking other ways to detect FSO radical. This involves both experiment and theory. The structure and spectroscopic properties of the ground ²A" state of FSO and its isomer, FOS, have been determined at the single and double excitation quadratic configuration interaction level of theory with a 6-311G(2d,f) Gaussian basis set. The local minimum corresponding to the isomer FOS lies about 84 kcal/mol above the global minimum structure corresponding to the FSO radical. A number of single-point QCISD calculations were performed with a small 6-311G* basis set to obtain qualitative features of the conformational potential energy surface for the isomerization FSO → FOS. Optimized geometries obtained for FSO are in excellent agreement with microwave spectroscopy data. A search for the electronic states of FSO is currently underway in our laboratory. The calculated results can be found in greater detail in an upcoming publication in the *Journal of Molecular Structure* (accepted).

II.4. Br₂SO

Photodissociation of Br₂SO following irradiation at 193 and 248 nm has been studied by laser induced fluorescence spectroscopy of the nascent SO fragment. The vibrational distributions for the nascent SO have been found to be inverted, suggesting a concerted mechanism for the dissociation at both wavelengths. A Franck Condon / Golden Rule model elucidates the geometry prior to the dissociation, suggesting the possibility that photodissociation at both wavelengths occurs via the same excited state of Br₂SO. The rotational and spin state distributions have been measured from rovibronically resolved spectra to support our discussion on the detailed dissociation mechanism. Quantum yield measurements suggest that other electronic states of the SO radical may be directly produced. This work will be published in *Chemical Physics Letters*.

II.5. (CH₃)₂SO

The photodissociation dynamics of the reaction, (CH₃)₂SO + hν(193 nm) → 2CH₃ + SO, have been examined by laser spectroscopic techniques. Relative vibrational and rotational state energy distributions of the nascent SO photofragment have been determined by using laser induced fluorescence spectroscopy on the (B³Σ⁻-X³Σ⁻) transition. The same technique has also been

employed to establish the quantum yield, $\Phi_{193}[\text{SO}(\text{X}^3\Sigma)] = 1.02 \pm 0.12$. The nascent vibrational state distributions in the v_1 and v_2 modes of the methyl radical have been determined by using 2+1 resonance enhanced multiphoton ionization spectroscopy via the $(3\text{p } ^2\text{A}_2'' \leftarrow 2\text{p } ^2\text{A}_2'')$ transition. These measurements were done in collaboration with M. Hawley and H.H. Nelson at the Naval Research Laboratory.

The energy distributions of the nascent fragments are best described by a concerted three-body fragmentation. While some of our data are suggestive of a concerted synchronous dissociation of the two S-C bonds in DMSO, we cannot conclusively determine the synchronicity from our results. Further studies of the photofragment angular distributions following 193 nm irradiation of dimethyl sulfoxide would be helpful in analyzing this aspect of the dissociation dynamics. This work appeared in the *Journal of Physical Chemistry* (J. Phys. Chem. 97, 1993, 12269).

II.6. $(\text{CH}_2)_2\text{SO}$

The photochemistry of ethylene episulfoxide, $(\text{CH}_2)_2\text{SO}$, has been investigated for the first time in our laboratory. Photodissociation of $(\text{CH}_2)_2\text{SO}$ at 193 and 248 nm produces $\text{SO}(v''=0-6)$ and $\text{SO}(v''=0-5)$, respectively. The vibrational state distributions of the SO photofragment are inverted with maxima at $v''=1$ in both cases. A Franck-Condon model and an impulsive model have been used to fit the experimentally observed vibrational state distributions and the internal energy content of the nascent $\text{SO}(\text{X}^3\Sigma)$ photofragment. These models are unable to fit the experimental observations, when the other fragment is ground state ethylene, but excellent correlation is obtained for the lowest energy triplet state of C_2H_4 . The time-dependent behavior of the $\text{SO}(\text{X}^3\Sigma)$ LIF signal has been measured, indicating a second ground state sulfur monoxide production pathway. The experimental $\text{SO}(\text{X}^3\Sigma)$ transients can be fit by a biexponential function. The slower production of $\text{SO}(\text{X}^3\Sigma)$ is believed to be due to relaxation of $\text{SO}(a^1\Delta)$, which is also produced in the photodissociation of $(\text{CH}_2)_2\text{SO}$. Quantum yields for the of $\text{SO}(a^1\Delta)$ and $\text{SO}(\text{X}^3\Sigma)$, based on a kinetic analysis, are 0.25 ± 0.02 and 0.41 ± 0.05 following 193 nm irradiation of $(\text{CH}_2)_2\text{SO}$, and 0.34 ± 0.03 and 0.44 ± 0.06 for the 248 nm photolysis. A manuscript of this work will be submitted to the *Journal of the American Chemical Society* in the near future.

II.7. $(\text{CH}_2)_3\text{SO}$

The photochemistry of trimethylene sulfoxide, $(\text{CH}_2)_3\text{SO}$, has been investigated in our laboratory. Photodissociation of $(\text{CH}_2)_3\text{SO}$ at 193 and 248 nm produces $\text{SO}(v''=0-6)$ and $\text{SO}(v''=0-6)$, respectively. The vibrational state distributions of the SO photofragment are inverted with maxima at $v''=1$ in both cases. A Franck-Condon model and an impulsive model have been used to fit the experimentally observed vibrational state distributions and the internal energy content of the nascent $\text{SO}(\text{X}^3\Sigma)$ photofragment. Both the Franck-Condon modelling of the vibrational state distributions and the impulsive modeling of the total internal energies of the photofragments, indicate that the photodissociation of trimethylene sulfoxide proceeds via a concerted fragmentation process to produce $\text{SO}(\text{X}^3\Sigma)$ and a trimethylene diradical. The two products are decoupled before the stable hydrocarbons, found in earlier product studies, are formed. The similar fragmentation products and the similar rotational temperatures in each vibrational level, as well as the similar inverted vibrational state distributions of the $\text{SO}(\text{X}^3\Sigma)$ photofragments for both 193 and 248 nm photolyses suggest that the dissociation occurs on the same potential surface. Best fit bond lengths, however, of the dressed SO molecule in the Franck-Condon model are found to be different for the 193 and 248 nm cases. The impulsive model calculation revealed that the values of the out-of-plane angle of the transition state of the trimethylene sulfoxide are also different at the two photolysis wavelengths. This result indicates that the geometries of the transition states are different for the 193 and 248 nm photolyses of the trimethylene sulfoxide. The UV absorption spectrum of $(\text{CH}_2)_3\text{SO}$ reveals that the 193 and 248 nm absorptions belong to different absorption bands. The dissociation most likely occurs on two different potential energy surfaces. This work is being prepared for submission in the *Journal of Physical Chemistry*.

II.8. $(\text{CH}_2)_4\text{SO}$

The 193 and 248 nm photodissociation of tetramethylene sulfoxide (TMSO) in the gas phase has been investigated by the same laser spectroscopy techniques as described above, and the vibrational state distributions of the nascent $\text{SO}(\text{X}^3\Sigma)$ photofragment have been measured at both wavelengths. These vibrational state distributions can be characterized as Boltzmann with vibrational temperatures of 1250 ± 60 and 1220 ± 60 K for the 193 and 248 nm photolyses respectively. Assuming that the SO photofragment is produced in concert with a 1,4-tetramethylene diradical, the

vibrational state distribution obtained in the 193 nm photolysis agrees well with an energy disposal model, in which the full reaction exoergicity is statistically partitioned among all the products' degrees of freedom. The quantum yield for SO($X^3\Sigma$) production at 193 nm, $\Phi_{SO(X)}^{193\text{ nm}} = 0.47 \pm 0.20$, has been obtained by comparison with SO₂ photolysis. For the 248 nm photodissociation, the experimentally obtained vibrational state distribution can be best described by a variant statistical model assuming three-body fragmentation, i.e. the products are an SO fragment and two ethylene molecules. The quantum yield for SO($X^3\Sigma$) production at 248 nm is $\Phi_{SO(X)}^{248\text{ nm}} = 0.44 \pm 0.19$. The OH photofragment has been detected during both the 193 and 248 nm photolyses of TMSO. The rotational state distributions of the OH($X^2\Pi, v''=0$) fragment have been determined by LIF spectroscopy using the A-X transition. The hydroxy rotational temperatures can be characterized as 600 ± 50 and 510 ± 40 K following photolysis of TMSO at 193 and 248 nm, respectively. The differences in the 193 and 248 nm photolyses can be explained if two different surfaces, i.e. a singlet and triplet, are advanced. For further details on this work, see the publication in the *Journal of Physical Chemistry* (J. Phys. Chem. 99, 1995, 17380).

II.9. C₆H₅NSO

The photochemistry of thionyl aniline has been examined for the first time. Photodissociation of C₆H₅NSO at 193 and 248 nm produces SO($v''=0-5$) and SO($v''=0-5$), respectively. The vibrational state distributions of the SO photofragment are inverted with maxima at $v''=1$ in both cases. A Franck-Condon model and an impulsive model have been used to fit the experimentally observed vibrational state distributions and the internal energy content of the nascent SO($X^3\Sigma$) photofragment. Both the Franck-Condon modelling of the vibrational state distributions and the impulsive modeling of the total internal energies of the photofragments, indicate that the photodissociation of trimethylene sulfoxide proceeds via a concerted fragmentation process to produce SO($X^3\Sigma$) and a phenyl nitrene species. A new spectrum in the range of 440-520 nm has been recorded. While early speculations believed that this was due to the ground state triplet of phenyl nitrene, we now believe that the dehydroazepine species is the carrier of the spectrum. The dissociation is believed to produce SO and singlet phenyl nitrene, which undergoes ring expansion to the dehydroazepine. This work is being prepared for submission to the *Journal of the American Chemical Society*.

II.10. C₂H₃O

State specific radiative lifetimes and electronic quenching cross-sections were measured for four different vibrational modes of CH₂CHO (\tilde{B}^2A''). Ground state vinoxy radicals were produced by 193nm excimer laser photolysis of CH₃OCH=CH₂, and pumped to the \tilde{B} state by a tunable dye laser operating between 332 and 348nm. Fluorescence decay rates were determined in the presence of twelve collision partners: He, Ar, N₂, O₂, CO, H₂, HCl, N₂O, CO₂, C₂H₄, CH₃OCH=CH₂ and SF₆. The measured electronic quenching cross-sections vary from 0.01 - 66.5 Å². Zero pressure radiative lifetimes are found to vary from 98±10 to 154±18 ns, depending on the vibrational mode. A resulting mechanism, consistent with all the observations, can be summarized into a kinetic model. For further details on the model, see the publication in the *Journal of Physical Chemistry* (J. Phys. Chem. 100, 1996, xxxx).

Recently, we have expanded our studies of the vinoxy radical, and we have observed LIF excitation spectra in a new region (316-330 nm). We have assigned transitions in this region to three vibrational modes: v_6 (OCH bend), v_5 (CH₂ scissor) and v_4 (CO stretch). Emission spectra have been obtained and assigned for the vibrational modes v_5 - v_9 . Based on these spectra, vibrational frequencies of these modes in the ground and excited states have been assigned. This work is being prepared for publication in *Chemical Physics Letters*.

II.11. O(³P) + OCS

The SO(X³Σ⁻) product vibrational and rotational distributions following the reaction of carbonyl sulfide (OCS) with O(³P) atom has been studied by laser-induced fluorescence spectroscopy on the B³Σ⁻ - X³Σ⁻ transition. The O(³P) atom was produced by 351 nm photolysis of NO₂. The nascent SO(X³Σ⁻) product vibrational state distribution was found to be inverted with a maximum at $v'' = 5$ and measurable population was detected up to $v'' = 10$. The rotational state distributions produced within 2 gas kinetic collisions can be characterized by an average rotational temperature, $T_R = 2200 \pm 400$ K. The observed SO(X³Σ⁻) internal energy accounts for 34% of the total energy available to the products. The non-statistical energy distribution in SO(X³Σ⁻) is consistent with an abstraction mechanism for the reaction. This work was recently published in *Chemical Physics Letters* (CPL 247, 1995, 313)

II.12. O(³P) + C₂H₄S

The SO(X³Σ⁻) product energy disposal in the desulfurization reaction of thiirane (C₂H₄S) with O(³P) atom has been studied by probing its rovibrational state distributions via laser-induced fluorescence spectroscopy on the B³Σ⁻ - X³Σ⁻ transition. The O(³P) atom was produced by 351 nm photolysis of NO₂. The nascent SO(X³Σ⁻) product vibrational state distribution was found to be inverted with a maximum at v" = 1 and measurable population was detected up to v" = 8. The rotational state distributions of SO(X³Σ⁻, v" = 1 - 5) produced within 2 gas kinetic collisions can be characterized by an average rotational temperature, T_R = 1163 ± 311 K. The observed SO(X³Σ⁻) internal energy accounts for 16% of the total energy available to the products. No evidence for the production of other species, e.g. OH, was observed. The non-statistical energy distribution in SO(X³Σ⁻) is consistent with an abstraction mechanism for the reaction. This work is currently in press in *Chemical Physics Letters*.

II.13. Rotational Distribution Modelling

Another area that we have been developing is a theoretical treatment of the nascent rotational state population distributions arising from photodissociation reactions. We have developed a kinematic distribution function to accurately reproduce the nascent rotational distributions of OH and SH following the photodissociations of H₂O and H₂S, respectively. This work was published in the *International Journal of Quantum Chemistry*. A second paper on isotope effects in photodissociation dynamics was published in *Chemical Physics Letters*. (CPL 211, 1993, 65)

In these works, a general procedure to evaluate the rotational state population distributions of the nascent photofragments from the photodissociation of polyatomic molecules has been implemented with the use of the kinematic distribution function developed by Chen and Pei.¹ Numerical evaluations of rotational state population distributions of diatomic photofragments from photodissociation of the general class of triatomic molecules are presented. We employ a semi-empirical model that utilizes a kinematic distribution function to calculate the rotational state population distributions of diatomic photofragments from the photodissociation of isotopically variant triatomic molecules. The numerically evaluated rotational distributions of the photofragments, SH

¹ K. Chen and C. Pei, *Chem. Phys. Lett.* **124**, 365 (1986)

and SD, are compared with experimental data on the nascent rotational state population distributions of the diatomic photofragments resulting from the laser photolysis of H₂S ($\lambda_{\text{photolysis}}=193, 222$ and 248 nm) and D₂S ($\lambda_{\text{photolysis}}=193$ and 222 nm).

In conclusion, the results clearly show that the kinematic distribution function, when used in conjunction with the experimental rotational state population distribution, can provide information about the degree of participation of different adiabatic surfaces in the presence of non-adiabatic coupling among them during a photochemical reaction. Even for the case of hydrogen sulfide photodissociation, where >98% of the available energy is partitioned into translational degrees of freedom, sensitive measurements of the internal energy distribution of the diatomic fragment provide a unique insight into the mechanisms of dissociation. This information not only helps unravel a detailed dissociative mechanism, but also gives information about the degree of non-adiabatic coupling between the two surfaces. Finally, the kinematic distribution model provides insight into the wavelength dependent photodissociation of H₂S, but we wish to *stress* that the true power of the model lies in systems of greater complexity where *ab initio* potentials are not available. For example, we have applied the model to study the nascent rotational distributions of sulfur monoxide deriving from the 193 nm photodissociation of SO₂.

III. PUBLICATIONS

17. Karl Matos, Ruben Delgado, Xirong Chen, Jeanne Hossenlopp and Brad R. Weiner, "*The Laser Photochemistry of Thionylaniline*", manuscript in preparation.
16. Fei Wu, Xirong Chen, and Brad R. Weiner, "*Photodissociation Dynamics of Trimethylene Sulfoxide*", manuscript in preparation.
15. Ruolian Wan, Xirong Chen, Katherine I. Barnhard, and Brad R. Weiner, *Observation of New Vibrational modes of the CH₂CHO Radical*", to be submitted to Chem. Phys. Lett.
14. Fei Wu, Xirong Chen and Brad R. Weiner, "*The Photochemistry of Ethylene Episulfoxide*", to be submitted to J. Am. Chem. Soc.
13. Xirong Chen, Fei Wu, Hongxin Wang and Brad R. Weiner, "*The 193 and 210 nm Photodissociation of Sulfur Dioxide*", to be submitted to J. Chem. Phys.
12. Hongxin Wang, Xirong Chen, Manuel A. Rivera and Brad R. Weiner, "*Photochemistry of Thionyl Bromide at 248 and 193 nm in the Gas Phase*", to be submitted to Chemical Physics
11. K. Ravichandaran, Yuchuan Gong, Fei Wu and Brad R. Weiner, "*SO(X³Σ) Product Energy Disposal in the Desulfurization Reaction of Thiirane with O(³P) Atoms*", Chem. Phys. Lett. **1996**, in press.
10. Luis A. Muñoz, Brad R. Weiner and Yasuyuki Ishikawa, "*Conformational Potential Energy Surface of the FSO Radical and its Isomer FOS in the Ground ²A" State*", J. Mol. Struct. **1996**, in press..
9. Katherine I. Barnhard, Min He and Brad R. Weiner, "*Excited State Dynamics of CH₂CHO(B²A')*", J. Phys. Chem. **100**, **1996**, xxxx.
8. Xirong Chen, Fei Wu and Brad R. Weiner, "*Internal State Distributions of SO(X³Σ) from the Reaction of O(³P) + OCS*", Chem. Phys. Lett. **247**, **1995**, 313.
7. Fei Wu, Xirong Chen and Brad R. Weiner, "*Photodissociation of Tetramethylene Sulfoxide at 193 and 248 nm in the Gas Phase*", J. Phys. Chem. **99**, **1995**, 17380.
6. Fei Wu, Xirong Chen and Brad R. Weiner, "*Photodissociation Studies of Cyclic Sulfoxides*", SPIE Proceedings (Laser Techniques for State-Selected and State-to-State Chemistry III), **2548**, **1995**, 355.
5. Katherine I. Barnhard, Min He and Brad R. Weiner, "*Radiative Lifetimes and Electronic State Quenching of CH₂CHO(B²A')*", SPIE Proceedings (Laser Techniques for State-Selected and State-to-State Chemistry III), **2548**, **1995**, 340.

4. Hongxin Wang, Xirong Chen and Brad R. Weiner, "*SO(X³Σ) Production from the 193 nm Laser Photolysis of Thionyl Fluoride*", Chem. Phys. Lett. 216, 1993, 537.
3. Xirong Chen, Hongxin Wang, Brad R. Weiner, Michael Hawley and H.H. Nelson, "*Photodissociation of Dimethyl Sulfoxide at 193 nm in the Gas Phase*", J. Phys. Chem. 97, 1993, 12269.
2. Hongxin Wang, Xirong Chen, and Brad R. Weiner, "*Laser Photodissociation Dynamics of Thionyl Chloride: Concerted and Stepwise Cleavage of S-Cl Bonds*", J. Phys. Chem. 97, 1993, 12260.
1. Xiaotian Gu, Luis A. Muñoz, Yasuyuki Ishikawa, and Brad R. Weiner, "*Isotope Effects and Wavelegth Dependence in the Rotational State Distributions of the Diatomic Photofragments, SH and SD, from the Photodissociation of H₂S and D₂S*", Chem. Phys. Lett. 211, 1993, 65.

IV. PERSONNEL

The following people have participated in this project in addition to the principal investigator.

Senior Personnel

Professor Xirong Chen from the Dalian Institute of Chemical Physics, Dalian, P.R. China, joined our research group in February, 1990.

Junior Personnel

Graduate Students

Katherine I. Barnhard (Department of Chemistry, Ph.D. expected August 1996)

Karl Matos (Department of Chemistry, Ph.D. expected May 1997)

Luis A. Muñoz (Chemical Physics Program)

Miriam Perez (Department of Chemistry, M.S. expected May 1996)

Ruolian Wan (Chemical Physics Program, M.S. expected May 1996)

Hongxin Wang (Chemical Physics Program; Ph.D. granted May 1993)

Fei Wu (Chemical Physics Program; Ph.D. expected March 1996)

Undergraduate Students

Harry Gómez (Department of Chemistry)

Stephen Gómez (Department of Chemistry)

Ruben Delgado (Department of Chemistry)

V. PRESENTATIONS

International / National (14)

14. *"Photodissociation Dynamics of Cyclic Sulfoxides"*
Fei Wu, Xirong Chen and Brad R. Weiner
Third Pan American Chemical Congress, San Juan, Puerto Rico, September 10-15, 1995
13. *"Radiative Lifetimes and Electronic State Quenching of CH₂CHO(B²A")"*
Katherine I. Barnhard, Ruolian Wan and Brad R. Weiner
Third Pan American Chemical Congress, San Juan, Puerto Rico, September 10-15, 1995
12. *"Photodissociation Dynamics of Cyclic Sulfoxides"*
Fei Wu, Xirong Chen and Brad R. Weiner
SPIE Laser Techniques for State-Selected and State-to-State Chemistry III, San Diego, California, July 1995
11. *"State-Resolved Fluorescence Quenching and Predissociation of the Vinoxy Radical: Evidence for Mode-Selective Bond-Scission"*
Katherine I. Barnhard, Ruolian Wan and Brad R. Weiner
SPIE Laser Techniques for State-Selected and State-to-State Chemistry III, San Diego, California, July 1995
10. *"The Laser Photchemistry of Thionylaniline"*
Karl Matos, Ruben Delgado, Xirong Chen, Jeanne Hossenlopp and Brad R. Weiner
50th Ohio State University International Symposium on Molecular Spectroscopy, Columbus, Ohio, June 1995
9. *"The Laser Photchemistry of Thionylaniline"*
Karl Matos, Ruben Delgado, Xirong Chen, Jeanne Hossenlopp and Brad R. Weiner
209th National Meeting of the American Chemical Society, Anaheim, California, 2-7 April 1995.
8. *"State-Resolved Distributions of Nascent SO(X³Σ, v") following SO₂ Photodissociation"*
Xirong Chen, Fei Wu, Hongxin Wang and Brad R. Weiner
10th Interdisciplinary Laser Science Conference, Dallas, Texas, 2-7 October 1994.
7. *"State-Resolved Predissociative Dynamics of the Vinoxy (CH₂CHO) Radical"*
Katherine I. Barnhard, Min He, Provi Mayo and Brad R. Weiner
10th Interdisciplinary Laser Science Conference, Dallas, Texas, 2-7 October 1994.
6. *"Energy Disposal as a Probe of the Ultraviolet Photodissociation Dynamics of Sulfur Dioxide".*
Fei Wu, Xirong Chen and Brad R. Weiner
1994 Gordon Research Conference on Atomic and Molecular Interactions, New London,

New Hampshire, 3-8 July 1994

5. *"Photochemistry of N-substituted thionylimides".*
Rubén Delgado, Karl Matos, Xirong Chen and Brad R. Weiner
207th National Meeting of the American Chemical Society, San Diego, California, 13-17 March 1994.
4. *"Photochemistry of Thionyl Bromide at 193 and 248 nm in the Gas Phase"*
Hongxin Wang, Xirong Chen and Brad R. Weiner
XVIth International Conference on Photochemistry, Vancouver, BC, Canada, 1-6 August 1993.
3. *"Structure and Spectroscopic Properties of the Photofragment, ClSO Radical and Its Isomer, ClOS, in the Ground 2A State"*
Gustavo E. Lopez, Brad R. Weiner and Yasuyuki Ishikawa
XVIth International Conference on Photochemistry, Vancouver, BC, Canada, 1-6 August 1993.
2. *"Three Body Photodissociation of Thionyl Chloride"*
Xirong Chen, Hongxin Wang and Brad R. Weiner
1993 Conference on the Dynamics of Molecular Collisions, Helen, Georgia, 6-11 June 1993.
1. *"The Photochemistry of Thionylaniline"*
K. Matos, X. Chen, H. Wang, and Brad R. Weiner
205th National Meeting of the American Chemical Society, Denver, Colorado, 29 March - 2 April 1993.

Universities and National Laboratories (6)

6. *"Energy Disposal as a Probe of Chemical Reaction Mechanisms"* (invited)
Brad R. Weiner
Department of Chemistry, Emory University, Atlanta, Georgia, 20 October 1995
5. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"* (invited)
Brad R. Weiner
Oak Ridge National Laboratories, Oak Ridge, Tennessee, 8 May 1995.
4. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"* (invited)
Brad R. Weiner
Department of Chemistry, University of Houston, Houston, Texas, 25 April 1995.
3. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"* (invited)
Brad R. Weiner

Department of Chemistry, Marquette University, Milwaukee, Wisconsin, 10 November 1993

2. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"* (invited)
Brad R. Weiner
Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 6 October 1993
1. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"* (invited)
Brad R. Weiner
Department of Chemistry, Tulane University, New Orleans, Louisiana, 1 February 1993

Regional (19)

19. *"Study of the Energy Disposal into the Diatomic Photofragments Following the Gas Phase Photodissociation of Cyclic Sulfoxides"*
Fei Wu, Xirong Chen, Yazmín Pedrogo and Brad R. Weiner
19th Annual ACS Senior Technical Meeting, Lajas, Puerto Rico, 3-4 November 1995.
18. *"Excited State Dynamics of the Vinoxy Radical B State"*
Katherine I. Barnhard, Ruolian Wan and Brad R. Weiner
19th Annual ACS Senior Technical Meeting, Lajas, Puerto Rico, 3-4 November 1995.
17. *"Bimolecular Dynamics: Examining Sulfur Atom Transfer Reactions in A+BCD - AB+CD Systems"*
Brad R. Weiner
19th Annual ACS Senior Technical Meeting, Lajas, Puerto Rico, 3-4 November 1995.
16. *"Intramolecular Vibrational Energy Redistribution within Excited Electronic States of the Vinoxy Radical"*
Ruolian Wan, Katherine I. Barnhard and Brad R. Weiner
30th Annual Junior Technical Meeting, Ponce, Puerto Rico, 4 March 1995.
15. *"The Laser Photchemistry of Thionylaniline"*
Karl Matos, Ruben Delgado, Xirong Chen, Jeanne Hossenlopp and Brad R. Weiner
30th Annual Junior Technical Meeting, Ponce, Puerto Rico, 4 March 1995.
14. *"Laser Photodissociation of SO₂ at 193 and 210 nm"*
Xirong Chen, Fei Wu, Hongxin Wang and Brad R. Weiner
Tropical Atmospheric Sciences Mini-Gordon Conference, Ponce, Puerto Rico, 24-25 February 1995
13. *"State-Resolved Fluorescence Lifetimes of the Vinoxy Radical: Evidence for Mode Selective Predissociation"*
Katherine I. Barnhard, Ruolian Wan and Brad R. Weiner

Tropical Atmospheric Sciences Mini-Gordon Conference, Ponce, Puerto Rico, 24-25 February 1995

12. *"State-Resolved Distributions of Nascent SO(X³Σ, ν") following SO₂ Photodissociation"*
Xirong Chen, Fei Wu, Hongxin Wang and Brad R. Weiner
18th Annual ACS Senior Technical Meeting, Aguadilla, Puerto Rico, 4-5 November 1994.
11. *"The Laser Photchemistry of Thionylaniline"*
Karl Matos, Ruben Delgado, Xirong Chen, Jeanne Hossenlopp and Brad R. Weiner
18th Annual ACS Senior Technical Meeting, Aguadilla, Puerto Rico, 4-5 November 1994.
10. *"State-resolved Fluorescence Quenching of CH₂CHO(B): Evidence for Mode-Selective Bond Scission"*
Katherine L. Barnhard, Ruolian Wan and Brad R. Weiner
18th Annual ACS Senior Technical Meeting, Aguadilla, Puerto Rico, 4-5 November 1994.
9. *"Nascent SO(X³Σ) Vibrational Distributions from the Photodissociation of Tetramethylene Sulfoxide at 193 and 248 nm"*
Fei Wu, Xirong Chen and Brad R. Weiner
18th Annual ACS Senior Technical Meeting, Aguadilla, Puerto Rico, 4-5 November 1994.
8. *"Dynamics of Sulfur Monoxide Photoelimination Reactions"*
B.R. Weiner
18th Annual ACS Senior Technical Meeting, Aguadilla, Puerto Rico, 4-5 November 1994.
7. *"The Relaxation of Spin State Population of Nascent SO(X³Σ) Following SO₂ Photodissociation at 193 nm".*
Ruolian Wan, Xirong Chen and Brad R. Weiner
29th Annual Junior Technical Meeting, Mayagüez, Puerto Rico, 5 March 1994.
6. *"Nascent SO(X³Σ) Vibrational Distributions from the Photodissociation of Tetramethylene Sulfoxide at 193 and 248 nm".*
Fei Wu, Xirong Chen and Brad R. Weiner
29th Annual Junior Technical Meeting, Mayagüez, Puerto Rico, 5 March 1994.
5. *"Nascent SO(X³Σ) Vibrational, Rotational and Spin State Distributions from the 193 nm Photodissociation of SO₂"*
Fei Wu, Xirong Chen, Yasuyuki Ishikawa and Brad R. Weiner
17th Annual ACS Senior Technical Meeting, Humacao, Puerto Rico, 5-6 November 1993
4. *"SO(X³Σ) Production from the 193 nm Laser Photolysis of Thionyl Fluoride"*
Hongxin Wang, Xirong Chen and Brad R. Weiner
17th Annual ACS Senior Technical Meeting, Humacao, Puerto Rico, 5-6 November 1993.
3. *"The Photochemistry of Thionylaniline"*

Brad R. Weiner

17th Annual ACS Senior Technical Meeting, Humacao, Puerto Rico, 5-6 November 1993.

2. *"Multiphoton Ionization Spectrum of SOCl₂ in a Supersonic Jet"*

Manuel A. Rivera, T. Yabe and Brad R. Weiner

28th Annual Junior Technical Meeting, Río Piedras, Puerto Rico, 6 March 1993

1. *"Vibrational Relaxation of Sulfur Monoxide Radicals at 298K"*

Félix M. Martínez, Xiaotian Gu and Brad R. Weiner

28th Annual Junior Technical Meeting, Río Piedras, Puerto Rico, 6 March 1993

VI. INTERACTIONS

Collaboration with Drs. H.H. Nelson and M. Hawley at the Chemistry Division, Naval Research Laboratory, Washington, D.C.

VII. SUMMARY

The majority of the objectives intended for this contract have been reached. The research effort at the University of Puerto Rico under this contract has produced significant results on the photodissociation dynamics of polyatomic molecules. A series of studies involving SO-containing polyatomic molecules has revealed interesting dynamical effects in the photo-induced production of sulfur monoxide. Several of these molecules warrant further study as model systems for three-body dissociations. A comparison of the photochemistry of cyclic sulfoxides has been carried out for the first time. A new model has been developed to calculate nascent rotational state distributions from the photodissociation of triatomic molecules. This model is now being applied to complicated systems that are not tractable by other methods. The detailed photophysics and spectroscopy of the vinoxy radical has been evaluated. The system provides an excellent model system for continued study of energy flow in excited states, as well as for photochemistry of free radicals.

This contract has established a strong viable research program in gas phase photochemistry, photophysics and spectroscopy at the University of Puerto Rico. The initiation of mainstream physical chemistry research in a minority institution, such as the University of Puerto Rico, provides a unique opportunity to increase underrepresented groups in this area of science. This resource has also led to an improvement in the educational environment for students, both graduate and undergraduate. This is primarily evidenced by students who have passed through this laboratory going on to work in mainstream laboratories *i.e.* University of California, University of Colorado, Cornell University, University of Wisconsin, Purdue University, Rice University, and University of Minnesota, for either their graduate or postdoctoral studies.

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APPENDICES